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II.

On the Alloys of Copper and Zinc.

BY FRANK H. STORER.

(Communicated November 9, 1859.)

THIS research was undertaken in order to ascertain what, if any, definite chemical compounds could be detected among the alloys of copper and zinc.

Several chemists had already been led to believe in the existence of two or more definite alloys, and at the commencement of my own labors I was strongly inclined to accept this view. A more extended investigation, however, has convinced me that no such definite compounds exist. On the contrary, I am confident that all the alloys of copper and zinc are simply isomorphous mixtures of the two metals, capable, as I shall proceed to show, of crystallizing at any point, from copper with only a trace of zinc, down to alloys containing but thirty per cent of copper, or even less, under favorable circumstances.

The misconceptions of previous observers* have evidently arisen either from the great tendency to separate into layers, instead of immediately forming a homogeneous mixture, which the metals exhibit when fused together; or from certain striking

* I must in this connection refer to, and except, the valuable memoir of Karsten (vid. Karsten u. v. Dechen's *Archiv für Mineralogie*, u. s. v. 1839, XII. 385), whose conclusions in regard to these alloys appear to be perfectly correct, with the exception of a few unimportant details. As is the case with the able research of the elder Mallet, the details of which are to be found only in the Report of the Tenth (Glasgow) Meeting of the British Association for the Advancement of Science, p. 258, the very meagre abstracts of this memoir which are given in the chemical journals and text-books fail to convey a correct idea of the results which have been obtained,—a fact which may serve to explain the ignorance which has been exhibited in regard to them by subsequent experimenters.

peculiarities of structure and of superficial coloration which occur among the different alloys. To these points I shall again allude.

The method which I have used in preparing the alloys has varied slightly according to the amount of copper contained in them. Those in which the proportion of copper was large were prepared by projecting granulated zinc by small portions into the molten copper, the crucible which contained it having been previously removed from the fire, the mixture being thoroughly stirred after each addition of zinc. This method succeeds very well when only a small amount of zinc is to be combined with the copper, perfect combination of the metals being readily obtained while the loss of zinc from volatilization, though considerable, is, if proper care be exercised, much less than would be at first sight supposed. But for alloys containing even as much as 50 or 55 per cent of zinc, this method becomes uncertain.

It is in this case necessary to bring the copper to a high degree of heat before adding the zinc; yet in spite of this precaution, and of the utmost care in adding the zinc only by small portions, which have previously been made as hot as possible, the mass contained in the crucible will often become chilled, and require to be again placed in the furnace in order to be remelted. Since the portion of zinc last added remains uncombined with the copper, and exposed at the surface of the mass, a great deal of it is lost during this operation.

In preparing alloys containing more than 50 per cent of zinc, I have melted the copper and zinc in separate crucibles, and have subsequently poured the zinc upon the copper. It is necessary to remove from the fire the crucible which contains the latter, and to cover it carefully, with the exception of a small opening through which the zinc may be poured; for violent ebullition and projection of particles of the melted metal occur during the first moments of combination. After thorough stirring* in either case, the mass was allowed to cool until a crust had formed on the surface of the alloy. This crust was then pierced, and the fluid matter beneath it poured out. The cup thus formed, having been removed from the crucible, was sawed in two, and portions of the crystals upon its sides cut off by means of a cold-chisel, for analysis. The sheets obtained from the fluid alloy poured off were also retained, and were subsequently analyzed.

The weight of alloy obtained in each experiment varied from two to six pounds. By operating in the manner described, it is easy—especially after a little practice

* I have found that a rod of soapstone eight or ten inches in length, cut somewhat tapering towards its point, screwed into a piece of ordinary one-inch iron gas-pipe, forms a very convenient stirrer. It should be ignited to expel moisture before being used.

has enabled one to judge when the crust is ready to be pierced — to obtain perfect cups lined with well-formed crystals.

The chief difficulty which presents itself depends upon the fact that the alloys containing more than 80 to 85 per cent of copper solidify much more rapidly on top than upon the sides or at the bottom of the crucible. It is therefore necessary to allow a very thick crust to form before piercing, or no cup at all will have been formed, and the alloy will flow out entirely in the fluid state, with the exception of the upper crust.

Fine cups are formed by all the alloys between 80 and 45 per cent of copper, the largest crystals being obtained when the crust is pierced while still quite thin; while the white alloys containing less than 40 per cent of copper solidify, if anything, more rapidly on the sides and at the bottom of the crucible, rendering it necessary to pour out what alloy is still fluid almost as soon as a crust begins to form on top. All the white alloys are liable to pass suddenly into a pasty plastic state similar to that assumed by zinc or by soft-solder while solidifying. On account of this peculiarity, it is exceedingly difficult to crystallize them. I have succeeded, however, in obtaining crystals of alloys as low down as 30 per cent of copper, and have no doubt that, by repeated trials, they might be obtained from alloys still richer in zinc.

These crystals are all octahedral, usually somewhat elongated and apparently much modified by the circumstances in which they have been formed. The edges of all of them are rounded. The octahedra are in general more largely developed upon one side than upon the other, apparently upon the side from which the last drippings of the melted metal fell. They are, moreover, combined together with parallel axes, which give to the crystals a striated appearance (see Figs. 1, 2, and 3); these striæ are not sharply defined, but their edges have the rounded character of the edges of the crystals. This general character is maintained throughout the whole series of crystals, from those of pure copper down to those of the lowest white alloys which I have obtained. No doubt can possibly be entertained of the complete resemblance of these crystals to each other throughout the series, while the striking similarity to the well-known crystals of pure copper (obtained by fusion) which they exhibit, strongly indicates that they belong to the regular system. As it is of course impossible to measure the angles of such crystals, they cannot be crystallographically determined; but the most obvious conclusion is, that they are monometric. This opinion, however, must be based rather upon analogy than on any distinct measurements.

Upon the assumption that the crystals which I have described belong to the

regular system, as well as upon the fact, which will appear in the sequel, that none of the crystals have been found to contain any larger quantity of either of their component metals than was contained in the remainder of the molten liquid from which they had separated, I have based my conclusion that the alloys of copper and zinc are isomorphous mixtures* of the two metals.

On this hypothesis it is of course presumed that both copper and zinc are capable of crystallizing in the regular system. Copper, as is well known, always occurs in forms of the monometric system. But in regard to zinc this has not been so satisfactorily proved. Not only, however, does analogy indicate that zinc should be monometric,—for, so far as is known, all the metals of the Three Series of Cooke† allied to it crystallize in forms of this system,—but Nicklès‡ has actually observed an instance in which it occurred in the form of pentagonal dodecahedrons.

I am well aware that this is an isolated example; that the angles of the crystals were not measured. It is not to be supposed, however, that a chemist so well versed in crystallography as M. Nicklès could have been mistaken regarding the form of his specimen. We know, moreover, from the analyses of Favre,§ that the zinc was almost absolutely pure. Gustav Rose|| has urged against this observation, that the form of the crystals is an improbable one, since no other instance is known of a metal crystallized in pentagonal dodecahedrons. I cannot myself perceive the force of this argument; few facts are more thoroughly established, than that the crystalline form of bodies may be largely modified by the influence of the circumstances under which they are formed,—witness, for example, the crystals of common salt obtained from solutions containing organic matter,¶ —while almost all the crystals of metals with which we are acquainted have been prepared by a single process,—igneous fusion.

Rose has also maintained that the crystals of Nicklès are similar to the rounded or irregularly crystallized masses formed in an atmosphere of zinc vapor which he

* It must not be supposed that this view supports in the least the idea of the older chemists, that alloys were mere "mixtures" of their component metals. For the experiments of Karsten (*loc. cit.*, S. 398, 400) have already shown that the comportment of the alloys of copper and zinc towards acids, and the solutions of various metallic salts, is that of chemical compounds, being entirely unlike that of a simple mechanical mixture of the two metals, or of a mixture of several alloys.

† Memoirs of American Academy, (New Series,) V. table to p. 256.

‡ Ann. Ch. et. Phys., (3.) XXII. 37.

§ Ibid., X. 170.

|| J. pr. Chem. (N. F.) LV. 292.

¶ Vid. Robin et Verdeil, *Traité de Chimie Anatomique*, (Paris, 1853,) II. 198, *et Atlas*, pl. 1.

has himself obtained from the receiving-vessels of the Silesian zinc furnaces, and which are, for that matter, familiar enough to those who have often had occasion to fuse zinc in covered crucibles. I would, however, suggest, that the circumstances under which these *mammelons* are formed are by no means identical with those in which Nicklès's crystals were prepared,* viz. in an atmosphere of hydrogen, at a lower heat, and doubtless with less rapid volatilization.†

On the other hand, the very fact which I have myself observed, namely, that most, and probably all, alloys of copper and zinc may be crystallized in octahedrons, is in itself strong presumptive evidence that zinc is capable of assuming a similar form. Indeed, in the absence of any marked tendency in these alloys to separate by eliquation, there remains no hypothesis other than that of isomorphous mixture by which to explain their composition.

* Vid. Jacquelain, *Ann. Ch. et Phys.* (3.) VII. 204; and Favre, *loc. cit.*

† I have endeavored to defend Nicklès's observation, the more especially because it is certainly as well entitled to be received by chemists as the experiments of Noeggerath (*Pogg. Ann.* XXXIX. 323) and Rose, which go to prove that zinc may crystallize in forms of the hexagonal system. Neither of these observers has analyzed the crystals which he has described, all of which were accidental products of smelting-works. Now we know from the researches of Cooke (*Memoirs of the American Academy*, New Series, V. 353; also, *Am. J. Sci.* (2.) XX. 225), that zinc, which contains only three or four per cent, and probably even a smaller quantity, of antimony, has a strong tendency to crystallize in the form of rhombic prisms of the compound Sb Zn_3 with excess of zinc. We have also the statements of Laurent and Holms (*Ann. Ch. et Phys.* 1835, (2.) LX. 333), that zinc containing three or four per cent of iron crystallizes in rhombic prisms; and of Warren de la Rue (*Phil. Mag. J.* (3.) XXVII. 370; also, *J. pr. Chem.* (N. F.) XXXVII. 126), who has obtained and measured rhombic prisms of composition,—

Zinc	90.00
Iron	2.56
Lead	6.00
Copper	1.44
									<hr/>
									100.00

A. Erdmann (*Berzelius, Traité*, II. 620) also has analyzed acicular crystals of zinc which were detached from a bit of distilled zinc which had been used to decompose a quantity of chloride of silver. These needles contained,—

Zinc	93.193
Iron	6.524
Lead	0.283
									<hr/>
									100.000

In view of all these data, showing the very great influence which the presence of a small amount of impurity may exert upon the crystalline form of zinc, the importance of the fact that we have no evidence whatsoever of the purity of the crystals described by Noeggerath and Rose is manifest.

I must observe in this connection, that G. Rose* has quite recently described a specimen of crystals, labelled "*Mengepresse*,"—a term applied to an alloy prepared from one pound of copper from Lauterberg, and two pounds of calamine,—which exists in the Royal Mineralogical Museum at Berlin, having been obtained from the collection of Klaproth. These crystals, in the opinion of Rose, appear to belong to the monometric system; but since Prof. Rose has published no analysis of them, we not only have no clew to their probable quantitative composition, but are left in doubt whether they are really a compound of copper and zinc; though the facts which I have here brought forward render the supposition an extremely probable one.

Notwithstanding this, and in spite of the fact that his alloy is only a single isolated example, Rose has urged, in direct opposition to his previous opinion, that it proves that zinc must belong to the regular system. In point of fact, however, the observation of Rose, taken by itself, evidently proves nothing of the kind. For, admitting that his crystals are really brass, he has offered no evidence to show that they do not belong to one of several possible definite alloys; only after proving that such crystals do occur through the whole series of alloys, as I have shown is really the case, and demonstrating that no definite compounds exist, could the idea of isomorphous mixture be entertained.

The crystals obtained by myself vary in size; some of them being more than half an inch in length, while others are quite minute. In general they are smallest in those instances where the greater part of the alloy had solidified before the crust was pierced.

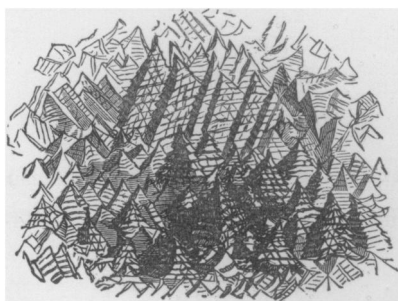


Fig. 1.

Fig. 1, which is a copy of a portion of the crystalline crust, from the alloy containing 94.38 per cent of copper, may serve to give a general idea of the character of these crystals.

In a few of the specimens of alloys, the crystals have exhibited a tendency to assume a somewhat tabular form,—a single face of an octahedron being largely developed, to the exclusion of the other faces, as may be seen in Fig. 2, *a*; while in other specimens separate individual crystals have occurred, Fig. 2, *b* and *c*. Both of these peculiarities presented themselves in the alloy of 83.72 per cent of copper, portions of which are represented in Fig. 2.

* Pogg. Ann., July, 1859, CVII. 448.

As a rule, however, all of the crystals obtained closely resemble those delineated in Fig. 1. Indeed, this figure might be used to represent almost any specimen in the long series of alloys which I have prepared. Very fine groups of crystals were obtained from those alloys which contained only one or two per cent of zinc. It is worthy of note, that, although these crystals have the same form and general appearance as those prepared by the same method from an equal quantity—three or four pounds—of pure copper, they are nevertheless much larger and more perfect. Since they may, for all practical purposes, be considered as crystals of copper with slight impurity of zinc, and are easily to be obtained, it would almost seem advisable to add one or two per cent of zinc to the metal employed in preparing specimens of crystallized copper for the cabinet. A similar case is presented by lead, which is very readily crystallized when it contains a little antimony: a fact well exemplified by the beautiful cups of crystals of *Krätzblei* which are prepared by partially cooling the metal in ladles, at the Frankensharner smelt-works near Clausthal, and doubtless at other localities in the Hartz.

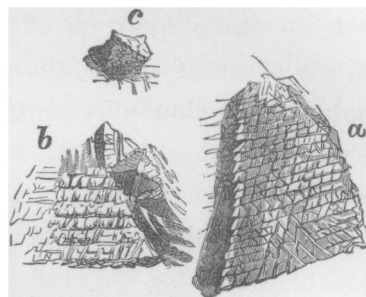


Fig. 2.

Since the crystals rich in copper which have just been described do not possess in any marked degree the yellow color peculiar to brass, they are somewhat less interesting than those obtained from alloys containing more zinc. Crystals of the latter can be obtained with the greatest ease by remelting old brass, or, better, by filling a Hessian crucible from the molten metal of the pots of a brass-founder, in which case all annoyance from the formation of a false crust of mixed oxide of zinc and metal is obviated. I mention these details, because I have myself found it somewhat difficult to acquire the knack of obtaining at will good crystals, when the alloys were prepared directly from the pure metals; having frequently been compelled to repeat a single experiment three or four times before satisfactory results were obtained. This is owing to the different degrees of rapidity with which the alloys cool, a fact to which I have already alluded.

The most perfect individual crystals were obtained from a quantity of brazier's solder which had been prepared at the foundry of the Revere Copper Company in Boston by fusing together 50 parts of copper with 50 parts of zinc. When an alloy of about this composition solidifies, and especially if it be suddenly cooled,—as happens when it is poured into iron ingot-moulds,—it assumes, as is well known, a highly crystalline structure, consisting almost entirely of a mass of coarse fibres

which shoot out from the points at which the alloy comes in contact with the cold metal of the mould. In the instances which have fallen under my notice, the ingots being from an inch to an inch and a half in depth, the fibres have shot up three quarters of an inch, or more, from the bottom of the ingot, leaving only a sheet of metal about a quarter of an inch in thickness on top, which had cooled more slowly by contact with the air.

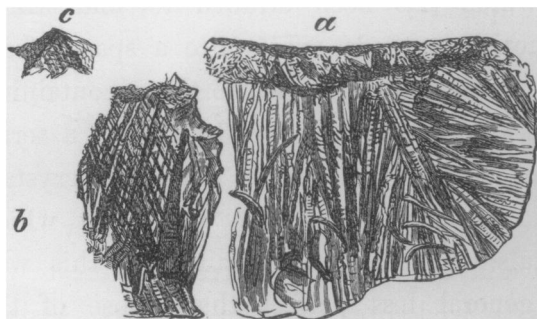


Fig. 3.

Fig. 3, *a*, represents in section a fragment of one of these ingots. One side—seen at the right—as well as the bottom of the portion figured having been in direct contact with the iron mould in which the ingot was cast, the crust just alluded to may also be seen above the fibres. On removing portions of this upper layer, its inferior surface will be found studded with

crystals, often of great beauty,— Fig. 3, *c* conveys but an imperfect idea of a portion of one of these,— while others frequently occur impacted among the fibres themselves. Indeed, these fibres, although described by Calvert and R. Johnson* as prismatic crystals, indicating that the alloy Cu Zn is a definite chemical compound, are evidently nothing more than collections of octohedral crystals, similar to those which form the fibres of sublimed sal-ammoniac and of several metals.†

By comparing the striations on these fibres with those upon any of the crystals of the series, it is impossible to resist the conviction that the former are mere aggregations. This conclusion is confirmed by the fact that the individual crystals which have been just mentioned as occurring above and among the fibres are evidently parts of the same system as the latter. Fig. 3, *b* represents a portion of one of the fibres somewhat magnified. It often happens that this alloy, known as brazier's solder, is run into cylindrical moulds of two or three inches in diameter, pierced in earth; in this case the fibres shoot out from all sides towards the centre, leaving at the middle of the bar a sort of neutral ground in which tolerably well-formed crystals frequently occur. The solder is prepared for market by warming it slightly, ‡

* Journal of the Franklin Institute, (3.) XXXVII. 200. See also Philosophical Transactions, Vol. CXLVIII. p. 367.

† *Vid.* Savart, Annales de Chimie et de Physique, (2.) XLI. 65.

‡ It must not be heated above a very moderate temperature, for, like metallic zinc at certain temperatures, it then becomes somewhat tenacious or pasty, and cannot be powdered.

and then pounding it in an iron mortar till it is reduced to a somewhat coarse powder. With the fibres, this result is easily obtained, since no great effort is necessary to tear asunder the numberless little crystals of which they are composed; but the larger individual crystals which occur in the crust and core, as just described, are much more refractory; they are removed from the finer powder by sifting, and are subsequently remelted. Among these rejected "kernels" very good crystals may often be found.

The tendency to shoot out into fibres, which has been alluded to, and which deserves something more than a passing notice, extends over quite a space, from alloys containing 57 or 58 per cent of copper, or even more, down to those containing 43 or 44 per cent, where it gradually disappears, as I have proved by casting a series of ingots. Although it does not altogether prevent one from obtaining crystals by the method of pouring off the still fluid portion of the alloy from that which has been allowed to solidify, still the crystals which I have obtained in this way within the limits of its influence are in general less perfect than those of the alloys containing more copper; indeed, on remelting the solder from which the finest separate crystals were obtained, and pouring off a portion of it after the rest had become solid, only indifferently good specimens could be procured. The alloy appearing to pass so quickly from the liquid to the solid state, that the crystals have but little time in which to form. It is remarkable that this inclination to form fibres is strongest in those alloys which contain nearly equal equivalents of zinc and copper, being less clearly marked as one recedes in either direction from this point, until a stringy texture analogous to that of copper is reached on the one hand, and the peculiar pastiness of zinc on the other. In preparing crystals, this pastiness manifests itself decidedly in the alloys immediately below those which are fibrous, becoming more strongly marked as the alloys are richer in zinc;—at least, so far as my own experiments have extended, i. e. to 30 per cent or less of copper. The fracture of these white alloys is for the most part vitreous. The pasty condition appears to depend to a certain extent on the manner in which the alloy is cooled, being less apparent when this process has been rapid. I have repeatedly obtained fine cups lined with tolerable crystals from alloys, which in other trials afforded nothing but a mass of paste. The transition, however, from complete liquidity to the pasty condition, when the latter is assumed, is very rapid.

The fact that the alloys just mentioned take on the fibrous texture when cooled under ordinary circumstances has, moreover, a very important practical bearing;—alloys at the upper limit of this fibrous tendency being the lowest—i. e. richest in zinc—which can be rolled or subjected to the various processes by which metals

are wrought. Singularly enough, at a point just beyond the limit at which the fibres cease to be apparent, viz. at 60 per cent of copper, an alloy of peculiar homogeneity occurs;—its fracture, as seen when small bars are broken, being smooth and compact, and entirely unlike either the coarse, irregular, stringy fracture of alloys richer in copper, or that of alloys containing only a little more zinc, upon the fracture of which small bundles of fine crystalline fibres are often apparent.

This alloy readily admits of being rolled, either hot or cold, and may be subjected to the operations of hammering or drawing without detriment, while alloys containing only a few per cent more copper can be rolled hot only when the sheets are raised to a very high temperature. Even then it is exceedingly difficult to obtain thin sheets without cracking their edges.

On the other hand, alloys containing somewhat less than 60 per cent of copper cannot well be rolled hot, since, when the ingots are heated, the exterior—especially at the corners—is liable to become pasty before the centre is soft enough to admit of being rolled.

In the preparation of the alloy of 60 per cent of copper, now so extensively used for sheathing vessels, under the name of Muntz's sheathing or yellow-metal,—also known as malleable brass,—it is the custom of founders to reserve a portion of the zinc which has been weighed out for a charge, until the alloy in their pots or furnace has become sufficiently hot;* the last portions of zinc are then added in small pieces, a sample of the alloy being tested after each such addition. This is done by dipping out a small portion of the melted mass and pouring it into a mould; a little ingot, five or six inches long by an inch or less in thickness, is thus obtained, which, after cooling, is broken on an anvil, and its fracture observed. If this does not exhibit a smooth and homogeneous surface, more zinc is added to the alloy. The accuracy with which an experienced workman can thus obtain the desired alloy is truly astonishing, the more especially since this homogeneous alloy is confined within very narrow limits.

It is stated by founders that the alloy of 60 per cent of copper and 40 per cent of zinc will present almost precisely the same homogeneity of fracture, whether the test ingot prepared from it be cooled slowly, by exposure to the air, or rapidly, by plung-

* The temperature to which the alloy is brought before pouring is considered to be a point of much importance by founders. In their opinion, a very inferior alloy would be formed if it were not heated much more strongly than would be necessary to maintain it in the liquid state. Compare Bolley, *Zur Kenntniss der Molecular-eigenschaften des Zinks*, Ann. Ch. u. Pharm., XCV. 302. This subject is evidently connected with the phenomena of tempering described in another part of this memoir.

ing it into cold water, while alloys containing either more or less than 60 per cent of copper are liable to assume different structures, according as they are cooled with greater or less rapidity. Two ingots are therefore sometimes cast, on each trial of the alloy, one of which is cooled in water and the other in air, for comparison. This double test is, however, deemed superfluous by skilful workmen.

I may remark, in this connection, that I have repeatedly obtained crystals, by the method of partial cooling, from portions of melted yellow-metal taken from the founder's pots at the moment it had afforded them a satisfactory test. These crystals are in no wise different from those obtained by myself from alloys of almost identical composition.

Although, as has been stated, the tendency to form fibres seems to have ceased at the alloy containing 60 per cent of copper, I cannot but think that the limit of its influence is less clearly defined than the "test" of yellow-metal founders would seem to indicate. In the circumstances under which this test is applied, it is doubtless true that no fibres are formed; but it is a matter of experience with manufacturers of yellow-metal, that the texture of the large ingots from which the sheets of sheathing are rolled is no longer so homogeneous as that of the small test ingot; they affirm also that this texture may vary greatly, according to the conditions in which the ingot is allowed to cool. It is evident, therefore, that during the processes of hot and cold rolling, and of annealing, to which the alloy is subsequently subjected, its texture may undergo various changes; while it is certain that the comparative durability of the sheathing, when exposed to the action of sea-water, must in great measure depend upon its relative compactness. If it be open and porous, as would be the case if a trace of the fibrous structure were present, it is clear that the sheathing would soon be destroyed;—not only because the salt water would come in contact with its interior portions, but also since the individual crystalline fibres of the alloy would doubtless resist its action more completely than the amorphous matter attached to them or contained in their interstices; from this a galvanic action would be produced, which could not fail to promote the corrosion of the alloy.

One of the most common complaints against yellow-metal arises from a tendency which some specimens of it exhibit to become so friable, after an exposure of longer or shorter duration to sea-water, that the sheets may readily be broken in pieces, sometimes even between the fingers. Attention has recently been called to this subject by Bobierre,* who would refer such cases more particularly to chemical

* Thèses présentées à la Faculté des Sciences de Paris.

Thèse de Physique: Des Phénomènes électro-chimiques qui caractérisent l'Altération, à la Mer, des Alliages employés pour doubler les Navires. Nantes: Imp. Busseuil. 1858. p. 61.

conditions depending, as he thinks, upon the too great proportion of zinc which is used in the preparation of the alloy, yellow-metal, as well as to changes of composition produced by hot rolling.

I cannot agree with this conclusion. In my own opinion, the other alternative which Bobierre has suggested, namely, peculiar arrangement of the molecules of which the alloy is composed, furnishes the true explanation of the difficulty. It is, however, possible, that at times, when the temperature of the reverberatory, in which the alloy is heated before passing to the rollers, is not properly regulated, zinc may be burned off from the exterior portions of the sheet, and that the alloy richer in copper which would thus be formed may subsequently be pressed into the body of the sheet during the operation of rolling. An alloy destitute of homogeneity would result from this treatment which could hardly be durable in any event. Instances of this sort must nevertheless be rare, for no part of the process is watched by the manufacturers more scrupulously than this.

It must also be borne in mind, that, of the enormous quantity of yellow-metal which is now used by the merchant-vessels of Great Britain and of this country, — all of which is composed of sixty parts of copper and forty parts of zinc, and rolled hot, — only a comparatively small portion passes into the friable condition to which I have alluded.

In most cases the alteration which the sheathing undergoes is gradual and regular, and the portion which remains after the wear of several years is still malleable. Indeed, the absolute amount of sheathing which becomes friable is entirely out of proportion with the annoyance to which it subjects ship-owners; * for it rarely happens, even in the worst instances, that more than one third of the sheets upon a vessel become friable, the remainder being in good condition.

The friability is therefore a purely accidental occurrence, and by no means a necessary consequence either of hot rolling or of the presence of 40 per cent of zinc in the alloy, as has been implied by Bobierre.† I am strongly of opinion, that it might be in every instance entirely obviated by methodically annealing or tempering

* Whenever the destruction of a portion of the sheathing requires that a ship be hauled up for repairs, it is customary, since this operation is an expensive one, to resheathe the vessel entirely; for as the friable sheets are interspersed among the others, and since all the sheets are somewhat worn, it would be bad economy to attempt any partial repairs. Of course the owner of the vessel regards the entire suit of sheathing as being worn out, and forms his opinion of the durability of yellow-metal in accordance with this view.

† Thèses, p. 77.

the sheets of alloy in such a manner that no fibres could form in them, and that their structure should be homogeneous.

Bobierre, in his very able thesis, to which I have already alluded, has urged that it would be well to discontinue the use of the alloy containing 60 per cent of copper, which admits of being rolled hot, and to substitute for it sheathing prepared from alloys containing about 66 per cent of copper, which can only be prepared by a most laborious process of cold rolling. It is true that the fibres which I have described would in this case probably never be encountered. Still there are several important objections to the proposition of M. Bobierre. Not only would the method of cold rolling consume a much greater amount of time and labor; but it would be exceedingly difficult, if not impossible, to procure any alloy the composition of which could be maintained so nearly constant as is the case with yellow-metal.* It is not probable that a test like the one applied to this alloy could be found anywhere else in the whole series.

It is frequently stated in chemical text-books that yellow-metal is always prepared from "best-selected" copper, and one is led to infer that a metal of peculiar purity is alone used in its manufacture. This may once have been the case; but since the immense increase in the use of this alloy, it would no longer be practicable to obtain a sufficient quantity of copper of uniform character, or indeed of any one kind, from which to prepare the large quantity of sheathing which is used. In an establishment where expense would be a secondary consideration, as, for example, in a government workshop, it might still be possible to prepare an alloy constantly from the same sorts of copper and of zinc, in which case, although the amount of zinc lost would probably be subject to considerable variations, one might, nevertheless, soon be able to control the process, and to prepare an alloy of the composition proposed by Bobierre, so that only trifling variations should occur in the composition of the product. But in ordinary practice manufacturers are compelled to make use of the most varied kinds of copper, not only because the supply of the best sorts is limited, but particularly from the fact, that, owing to the competition which exists between the various founderies, — or rather, by force of the laws which regulate supply and demand, — they are obliged to remelt larger quantities of old copper sheathing,† the origin of which is unknown to them, and which may have been originally prepared from copper of inferior quality.

* An alloy of constant composition might, however, possibly be prepared, by adding known quantities of melted copper to determined volumes of molten yellow-metal which had been prepared by the usual method.

† The popular notion, that a better — "more compact" — product is obtained by *remelting* any alloy, may also have some connection with this custom.

Now since many of the impurities of copper are eliminated when it unites with zinc, being thrown up on the surface of the melted metal as a crust or scum, which is removed by the workmen,* and as no two samples of copper contain the same kind or quantity of impurity, the amount of it removed, or, what is the same thing, the amount of copper left to unite with a given weight of zinc,† must continually vary.

From this it may easily be seen how very difficult, if not impracticable, it would be to obtain anything like constant results, unless some test were found by which the workmen might ascertain at least approximately the composition of his alloy.‡

That it is of the first importance that every alloy used for sheathing shall possess some one constant composition, so that it may endure equally well on all parts of the vessel, and that no galvanic action may occur between the metal of different sheets, is a point too obvious to be mentioned.

It might still be urged against yellow-metal, that the admixture of other metals — of kinds capable of mingling with it — which may have been derived from the copper used in its preparation, is a serious objection to its use. This is true, and the remark applies with equal or even greater force to all the alloys used for sheathing; it must always depend upon the condition of copper metallurgy. It would apply more forcibly, for example, to the low-grade brass which Bobierre has proposed to substitute for the ordinary sheathing-metal; for since the “test” by means of which founders are enabled to prepare the alloy — yellow-metal — of constant composition cannot be obtained if metals are present which are incapable of mixing in all proportions with this alloy, in which event small particles of the foreign substances would be found irregularly disseminated upon the fractured surface of the test ingot, manufacturers are enabled to ascertain at once whether or no a given sample of copper is suitable for the preparation of yellow-metal. Whenever it is

* This explains the remark of Karsten (*loc. cit.*, S. 386), that perfectly pure copper can take up from 1.5 to 2.5 per cent more zinc than impure, and still afford a product of better color, more tenacious and more malleable.

† Much zinc also is lost in this case, both by alloying with the foreign metal and by uniting with any oxygen which may have been combined with the latter. As the workmen say, impure copper “burns up” a great deal of zinc.

‡ It must be well understood, however, that as a rule manufacturers of alloys of copper and zinc always use the best copper they can obtain, since it is generally more economical for them to do so. For the purer this metal is, so much the greater will be the total amount of alloy obtained by the use of a given weight of it, or, in other words, the loss, mentioned in the preceding notes, which would occur from elimination of impurities, will be smaller.

found that satisfactory tests cannot be obtained, the copper is immediately rejected by the founders, and applied to some other use. No similar means of controlling the purity of the brass in question are known.

It does not appear—at all events it has never been proved—that any serious injury results in practice from the use of the most varied kinds of copper, so long as they afford the desired *homogeneous* alloy containing 40 per cent of zinc.

I do not wish to deny that hurtful impurities may at times occur in yellow-metal, in spite of the test to which I have so frequently alluded. Most probably the very rare cases in which this alloy wears out irregularly, portions of the sheet being much corroded, while other parts are scarcely at all acted upon and have preserved their original color and malleability, may be referred to the irregular diffusion of such impurities throughout the mass of alloy of which the sheet was formed;* but their influence must be regarded as being of very slight importance in comparison with the changes of structure which have already been discussed.

The following is a list of the alloys which I have prepared. Crystals were obtained from all of them, with the exception perhaps of one or two of those lowest in the series, where the tendency to assume a pasty state during solidification renders the crystallization obscure.

The amount of copper contained in both the crystals and the portion of fluid alloy poured off from above them was determined directly by assay in each instance. The copper used in the preparation of the alloys was a very pure article from Lake Superior; it contained only a certain amount of suboxide of copper and traces of silver.

The zinc was from La Vieille Montaigne, containing as its principal impurity a small amount of lead. Both metals were granulated for convenience in weighing. The lead and other impurities have been neglected in stating my results.

* It is not impossible that the small amount of silver which, as is well known, is precipitated from sea-water upon the metallic sheathing of ships, can accumulate to such an extent in yellow-metal which has been repeatedly used and remelted, that the durability of the latter may be seriously impaired thereby. It is, however, equally probable, and perhaps more so, that the greater part of this silver is eliminated in the preparation of the alloy, when the old metal is fused with zinc.

Number of the Experiment.	Per cent of Copper put into the Alloy.	Per cent of Copper found in the Crystals.	Per cent of Copper found in the portion of Alloy poured off.	Number of the Experiment.	Per cent of Copper put into the Alloy.	Per cent of Copper found in the Crystals.	Per cent of Copper found in the portion of Alloy poured off.
1	97.38	99.14	98.68	21*			62.30
2	96.50	95.57	97.40	22	60.29	61.16	61.99
3	94.38	95.06	95.04	23†		60.92	61.36
4	94.38	94.30	93.82	24†		60.77	60.88
5	91.38	90.77	91.49	25‡		60.42	60.24
6	88.38	88.86	88.78	26	56.69	57.82	58.66
7	85.38	86.10	85.74	27	53.09	54.22	54.45
8	79.38	83.72	83.61	28	51.00	52.62	52.11
9	82.38	82.89	82.52	29	49.00	49.51	49.55
10	79.38	80.34	80.73	30	47.00	49.43	48.26
11	76.38	77.32	78.92	31	45.00	47.49	46.79
12	73.38	75.03	74.27	32	43.00	44.41	43.63
13	74.38	75.71	74.94	33*		43.64	44.01
14	72.38	74.52	73.61	34	41.00	41.48	42.19
15	70.00	71.48	71.68	35	39.00	38.57	38.77
16*			69.20	36	37.00	38.09	37.71
17	67.40	68.93	67.37	37	35.00	35.33	36.71
18	65.94	67.12		38	33.00	32.98	32.79
19*		66.94		39	27.31	29.67	29.07
20*		65.56		40*		29.07	

In determining the amounts of copper contained in these alloys I have employed a method which has been used for a long time by many of the copper assayers of this country, by whom it is highly esteemed. It is essentially the old Swedish method§ of precipitating the copper from its solution in acid, by means of metallic iron; with, however, several more modern modifications and improvements.|| Since several of the details of this process have never, to my knowledge, appeared in chemical literature, I shall make no apology for describing it at length in this connection.

In choosing samples of the alloy for analysis, I have been careful to select those portions of the cup which were best crystallized, avoiding always the upper crust,

* The instances in which the amounts of metal used in preparing the alloy are not given, refer to crystallized products which were obtained accidentally during the course of the research.

† Yellow-metal from founder's pots, said, from appearance of test ingot, to require a little more zinc.

‡ Yellow-metal which had afforded a satisfactory test.

§ *Vid.* Bergman, Physical and Chemical Essays, translated from the original Latin by E. Cullen, M. D., (London, 1788,) Vol. II. p. 443. Described more fully by Kersten, in Karsten u. von Dechen's *Archiv für Mineralogie, u. s. w.*, XII. 567; also by Kerl, in Bodemann's *Probirkunst* von Bruno Kerl, (Clausthal, 1857,) S. 216.

|| For information concerning these I am indebted to Mr. G. J. Dickinson, chemist of the copper works at Point Shirley, near Boston.

which had lost zinc by volatilization while cooling; from the sheets into which the fluid portion of the alloy was cast, I have taken pieces near the edge, which were free from any admixture of fragments of the crust.

Pieces of the alloy weighing from four to twelve grammes, accordingly as they contained a greater or less amount of copper, which had been carefully cleaned by filing and brushing, were placed in covered porcelain dishes, and dissolved in strong nitric acid on the sand-bath, the usual precautions to avoid loss from spattering being observed. To the solution thus obtained, sulphuric acid—which had been freed from its impurity of lead by dilution with water and subsequent partial concentration—was added, and the mixture evaporated to dryness over the water-bath; more sulphuric acid being added, and the solution again evaporated until all the nitric acid was expelled, or till no trace of blue crystals remained. I have rarely found it necessary to evaporate the solution more than twice in order to effect this.

It is of importance that the nitric acid shall be thoroughly removed, for in the presence even of a mere trace of this acid it is exceedingly difficult to precipitate, by means of iron, the last portions of copper from its solution.

After all the nitric acid had been expelled, the mixed sulphates were dissolved in hot water, and the sulphate of lead (from impurity in the zinc of the alloy) allowed to settle; this was then separated and washed with acidulated water, by decantation.

The solution, which had been collected in a capacious beaker, was now largely diluted with water and placed upon a sand-bath, the heat of which was regulated so that the solution could attain a temperature nearly equal to boiling, without, however, coming into actual ebullition. A sheet of the purest iron obtainable was next placed in the solution, leaning against the sides of the beaker so that the largest possible amount of its surface should be exposed, in order that the iron might be attacked equally at all points by the acid, and that the copper should be precipitated in even sheets upon it.

The solution should be acid enough to insure a slight evolution of hydrogen during the precipitation. Care should, however, be taken to guard, in the first instance, against the addition of too great an excess of acid, lest the iron be corroded to an unnecessary or even ruinous extent. It is of course desirable to avoid dissolving any more iron than is necessary to insure regularity and completeness in the precipitation, for in this case a smaller portion of its impurities will be exposed, and its surface will remain smoother.

After the introduction of the iron, the beaker is to be covered with a glass plate, and left to itself until the copper is entirely precipitated, which occurs at the end of an hour or two at farthest. Having proved that no more copper is contained in the solution by testing a small portion of it with sulphuretted-hydrogen water, the beaker is removed from the sand-bath, and the clear acid solution decanted off as completely as possible from the copper and iron.

If this solution be diluted with a large quantity of hot water, it immediately becomes yellow, then turbid, and in a few minutes deposits a bulky flocculent precipitate of a basic salt of peroxide of iron, although the supernatant liquid is strongly acid. Since a quantity of this solution remains adhering to the metals, it is well, in order to avoid the precipitate which would form if they were treated at once with hot water, first to pour a small quantity of cold water upon them. The piece of iron is then to be taken from the beaker, and any particles of copper which may be loosely attached to it removed by means of the wash-bottle; the iron being carefully preserved for subsequent examination. The copper, having been once more rinsed with cold water, is now to be treated with boiling water, which should be decanted off into a large clean beaker, without waiting for all the copper to be deposited, as soon as the liquor assumes a yellow color. After two or three additions of hot water, the subsalt of iron is no longer precipitated, and the copper may be allowed to subside at its leisure. Any particles of copper which are found adhering to the sheet of iron which was used for the precipitation must now be removed by gently rubbing them with the finger, care being taken not to disturb the black coat* which is found adhering to the iron, any more than can be avoided; they are then to be washed into a small porcelain capsule, into which is also brought the mixed deposit of subsalt of iron and particles of copper collected during the first rapid washing of the copper.

* The black crust which forms on the iron beneath the layer of copper contains a small amount of carbon and some silica, but consists for the most part of what appears to be a compound of silicic acid and oxide of iron; this substance, called Slag by Morfit and Booth in their very able "Report upon the Chemical Analysis of Cast-Iron Gun-Metal," (*vid.* Report of Experiments on Strength, &c. of Metals for Cannon, by Officers of the Ordnance Department, U. S. Army, (Philadelphia, Baird, 1856, 4to,) p. 408,) is but sparingly soluble in dilute chlorhydric acid; slowly soluble in cold, more rapidly in hot concentrated chlorhydric acid; easily soluble in concentrated nitric acid, especially when hot; with separation of silica in both cases. It is slowly decomposed by strong soda lye. This "slag" is formed in considerably larger quantity when sulphuric acid is used than when chlorhydric acid is substituted for it in the assay. As it usually adheres, however, to the iron with considerable firmness, the copper can generally be rubbed off without disturbing it materially.

The contents of the capsule are now treated with dilute chlorhydric acid, in which the subsalt is readily soluble, washed with water, and added to the original copper, the washing of which is to be continued till the last traces of acid are removed. The copper, having been transferred to a porcelain boat, was dried at 100° C., ignited in a current of hydrogen gas, and subsequently weighed.

The iron used in these assays was that known as the "best Russia sheet." In order to obtain the best possible pieces, I have followed the custom of copper assayers in allowing a sheet-iron worker to cut up a number of pounds of Russia sheet into bits of about two and a half by three and a half inches, this size having been found well adapted to the work at hand, smaller pieces being unequally corroded; from this supply only those pieces which presented a perfectly smooth and even surface were selected for use. Those pieces which are at all corrugated or uneven ought to be rejected, for such are acted on unequally by the acid, and copper would be lost in the cavities thus formed.

Since the sharp angles of these rectangular bits of iron are liable to be corroded very much by the acid, in which case particles of iron might drop off and contaminate the copper, it is best to remove them by means of a rasp, and to make the corners round and smooth.

The glazed coating which occurs upon the surface of Russian sheet-iron, and which, according to Wells,* consists of silicate of iron, is readily removed by digestion in moderately dilute chlorhydric acid, in which it soon falls off in flakes. After washing with water, the bits of iron are dried and preserved for use.

In conducting the assay it is of importance that the solution should be dilute, since the precipitation of the copper in this case goes on more regularly, and is sooner completed; it should be warm, not only that the copper may be precipitated more rapidly, but in order to avoid the formation of a basic iron salt, which is very liable to contaminate the copper when it is precipitated in the cold. This basic salt frequently forms during the precipitation, even in warm solutions, if they are not sufficiently acidulated. If a solution be at the same time somewhat concentrated, and not sufficiently acid, it often happens that a portion of the copper becomes so firmly attached to the iron that it cannot be rubbed off. This accident will rarely occur, however, to any one accustomed to the assay.

It is remarkable that no one who has written upon this process has, so far as I can ascertain, appreciated the necessity of igniting the dry copper in a current

* Proceedings of Boston Society of Natural History, IV. 296.

of hydrogen before weighing it. That this operation is of the first importance is, however, well known to the analysts of this vicinity, who have long been accustomed to apply it in practice.* It is necessitated less, as it appears to me, by the oxide of copper formed during drying,—for the bright surfaces of the copper precipitated by this method remain untarnished when rapidly dried at temperatures even as high as 110° to 115° ,—than by an impurity consisting of organic matter derived from the iron; either carbon, or perhaps some one of the offensive hydro-carbons which are generated during the action of acids upon iron, which may adhere to the spongy copper. At all events, if a portion of the precipitated copper which has been dried at 100° —or at any temperature lower than that at which oxidation occurs—be placed, as was suggested to me by Mr. Dickinson, in a bulb tube with narrow outlet, such as is used in testing for arsenic, and heated in the flame of a spirit-lamp, it will be found that a quantity of water collects in the narrow part of the tube, while the copper becomes lustrous and assumes the bright red color proper to it. At first sight it would appear as if this behavior was produced by the reaction of a portion of the spongy copper upon the oxide of copper with which it might be soiled, in which event a small quantity of suboxide of copper would be formed, the color of which could hardly mask, to any extent, that of the pure copper. But on examining the reaction more attentively I have found that carbonic acid as well as water can readily be detected in the atmosphere expelled from the tube in which the copper is heated; a distinct empyreumatic odor is at the same time perceptible. I have also several times observed traces of ammonia. This gas is always evolved in considerable quantity when the dirty copper is heated in an atmosphere of hydrogen; the aqueous vapor driven off in this case being strongly alkaline from its presence. Organic matter must therefore have been attached to the spongy copper, and the lustre which the latter acquired when heated may have been occasioned by the simple expulsion of the impurity, or in part by the reduction of oxide of copper by it.

That the phenomenon does not depend upon the presence of free carbon seems to be proved by the fact that portions from the exterior of a mass of spongy copper, which had been protected from contact with the iron by a layer of copper nearly an inch in thickness, were found to exhibit reactions similar to those just described, water and empyreuma being evolved when the dry copper was heated in a closed tube. Indeed,

* In lieu of this, some assayers convert the precipitated copper into oxide, and weigh the latter.

the formation of water in any case in Mr. Dickinson's experiment with the arsenic-tube is an insuperable objection to this explanation, as well as to the idea that mixed copper and oxide of copper have reacted upon each other.

I have determined the quantity of this impurity in some fifty or sixty instances: it was found to vary from 1.5 per cent or less to 4 or even 5 per cent, in exceptional cases, of the copper dried at 100°; ordinarily it was from 2 to 2.5 per cent. These remarks refer to copper precipitated from sulphuric acid solutions, which is usually in a porous spongy state. When precipitated from chlorhydric acid solutions, it is usually crystalline and compact, and doubtless contains less impurity. It is said, however, that a certain amount of loss will invariably occur, even when the best samples of copper precipitated by iron are heated in an atmosphere of hydrogen. Even in copper precipitated by pure zinc I have observed that an appreciable loss occurs, — varying in my experiments from 0.5 to 2 per cent of the dry copper, — when it is ignited in hydrogen gas. It would appear that, while copper may be determined with great accuracy when precipitated by pure zinc in a platinum vessel, as recommended by Fresenius,* even when the precipitate is dried only at 100°, for in this case the copper is deposited in a condition so compact that little or no impurity can adhere to or oxide form upon it, yet it can hardly be determined with nicety when precipitated in the spongy state, unless it be ignited in a current of hydrogen, or converted into oxide before weighing; it is necessary also to exercise the greatest care that none of the smaller particles of copper, are lost during the washing, for many samples of copper, when precipitated as sponge by zinc, are peculiarly liable to this accident.

In regard to the assay which I have attempted to describe, I would remark that I have used iron instead of zinc,† simply because I was, at the time, unable to procure a sufficient quantity of the latter in a state pure enough for analytical purposes. The assay by iron, as I have used it, is clearly not an accurate analytical process, but, on the other hand, it is in several respects preferable — as an assay — to the method by zinc, and will be found, after a little practice, to yield satisfactory results. It is doubtless as good a method as any which we possess, wherever absolute accuracy is not required, and where a large number of determinations must be made. Admitting that the results obtained by it may vary among themselves within the limits of one per cent, or in exceptional cases even to the extent of one

* *Anleitung zur Quantitative chemischen Analyse*, (Braunschweig, 1858,) S. 247.

† Method proposed by Vauquelin, *Annales de Chimie*, (1798,) XXVIII. 50.

and a half per cent, I have still deemed it sufficiently accurate for the work to which I have applied it; for it must be remembered that these differences are much smaller than the variations in composition which may occur in different parts of the same cup of alloy, from partial volatilization of the zinc, or from incomplete mixture of the metals of which it is composed.

I may also remark, that although this assay was not adopted by myself until after thorough trial of several other processes which seemed to be applicable to the special case with which I was occupied, I now consider it a very valuable method.

It deserves mention in this connection, that the assay by iron has been entirely misunderstood by some writers. Thus, Mitchell* directs that the whole of the iron added shall be dissolved in chlorhydric acid, just as if it were zinc, after the copper has been completely precipitated; the absurdity of which procedure is manifest.

In concluding the subject, I may observe that American assayers are accustomed in practice to use a mixture of nitric and chlorhydric acids as a solvent in the first instance of the sample to be assayed, and to expel the nitric acid by evaporating twice to dryness with an excess of chlorhydric acid. The copper being then precipitated from the hot chlorhydric solution. Some of them collect the copper upon a filter, instead of washing by decantation, and rinse it once or twice with very dilute chlorhydric acid before washing with water.

This process has the advantage, that a larger portion of the impurity of the iron is soluble in chlorhydric than in sulphuric acid, hence there is less chance of the copper being contaminated by it; basic iron salts are also less liable to form; the evaporations, which are conducted over the sand-bath, consume somewhat less time than when sulphuric acid is used; and the copper, being precipitated in a crystalline state, is easily washed without loss, and is not liable to be attacked by the acid solution.†

On the other hand, in the process by sulphuric acid, — which I have used merely in order to remove the lead which is contained in the alloys, — the last traces of copper seem to be somewhat more readily precipitated from the solution, and the accident of the copper adhering too closely to the iron occurs, perhaps, more rarely.

Of the special precautions which must be taken when this assay is applied to

* Manual of Pract. Assaying, (London, Baillière, 1854,) p. 257.

† The assay undoubtedly affords more accurate results with chlorhydric acid than when sulphuric acid is used. Mr. Dickinson assures me, that in his hands variations so great as 0.5 per cent are entirely exceptional, the usual difference between any two assays of a homogeneous sample of ore not being larger than 0.2 to 0.3 per cent.

the various impure ores of copper, I cannot here speak. Many of them have been already described by Kerl.* I would, however, mention the fact, that, in cases where arsenic is the only impurity, it has been found advantageous in practice to precipitate it upon iron with the copper, and to expel it subsequently when the latter is heated in the atmosphere of hydrogen.

It is a well-known fact, that the combination of copper with zinc is attended with ebullition of considerable violence, so that portions of the melted mass are often thrown to a distance of several feet from the crucible. Yet it does not appear to have been previously noticed by chemists, that this action is much more energetic while the first portions of zinc are being added to the copper, and that the loss of zinc by volatilization is far greater at this time than at any subsequent stage of the operation; indeed, when the alloy has become somewhat rich in zinc, it takes up an additional portion so quietly, that scarcely any action is to be observed. The fact is, however, well known to brass-founders, who are in the habit of first melting a quantity of old brass with the copper in their crucibles before adding any zinc as such.

A very violent action will also occur, if, after allowing the zinc to melt and remain floating above the copper, as it will do if the mass is not agitated after each addition of zinc, the two metals are suddenly stirred together. This action is apparently analogous to that observed by Levol,† which occurs when layers of melted silver and gold are mixed. Levol ascribes the violent ebullition which ensues when these metals are stirred together to the escape of oxygen which had been absorbed by the molten silver, and which would be expelled as soon as this metal unites with the gold. This hypothesis, however, does not in my opinion satisfactorily explain the phenomena which occur in the case of copper and zinc. Another explanation is afforded by the experiments of Person,‡ who has shown that in the formation of certain alloys a large amount of latent heat is evolved.

The apparent energy with which the combination of copper and zinc occurs, is often mentioned in treatises on chemistry, as if it indicated the existence of strong chemical affinity between the two metals. Yet it is easy to separate the zinc completely from any of these alloys by heat. Indeed, Bobierre§ has devised a method

* *Op. cit.*, S. 219.

† *Ann. Ch. et Phys.*, (3.) XXXIX. 168.

‡ *Ibid.*, XXIV. 146.

§ *Thèses*, p. 57; also, *Compt. Rend.*, XXXVI. 224.

for their quantitative analysis, by heating the sample of alloy in a porcelain tube, through which a current of hydrogen is made to flow.

In preparing the alloys, it may readily happen, if the mass be not very frequently stirred, that a small portion of the copper, or of an alloy rich in copper, may become chilled and solidify at the bottom of the crucible, while a quantity of easily fusible alloy, rich in zinc, has formed and remains liquid above it. Accidents of this nature happened to myself very frequently during the earlier part of the research. They occasioned no inconsiderable loss of time, since it was in every instance necessary to prepare a new sample of the alloy on account of the enormous waste of zinc which would occur if one attempted to remelt the chilled *culot*; and were especially vexatious, from seeming to indicate the existence of definite alloys having little or no affinity for each other. Similar accidents sometimes occur in brass-foundries, but are evidently less liable to take place here, where the amount of melted metal is large and the heat well regulated, than in the small crucibles and furnaces of the chemical laboratory. It is worthy of remark, that many brass-founders refer them to some peculiarity of the particular sample of copper used. If any trouble of this kind is experienced, a portion of common salt is usually thrown into the crucible, it being regarded as a remedy. It is very probable that the presence of some foreign metal may prevent or retard combination; on the other hand, copper which still contains a portion of sulphur is thought to combine with zinc with peculiar facility. In my own experiments these occurrences appeared to depend entirely upon irregular heating of the furnace, or upon insufficient stirring. D. Forbes* has analyzed such specimens which were produced accidentally in the ordinary process of brass-making. They consisted of a white alloy containing 46.51 per cent of copper, and of a yellow alloy containing 56.91 per cent of copper. From my own experience, I am satisfied that layers containing almost any proportion of the two metals may form.

It is doubtless this tendency of the metals to remain unmixed in separate layers, when not subjected to agitation, which has led several chemists to believe that the alloys of copper and zinc are apt to separate by eliquation into two portions respectively rich in copper and in zinc; from which they have inferred, as I have previously remarked, the existence of definite compounds. Although in my own experiments I have been unable to detect any eliquation, I would by no means

* Report of 24th (Liverpool) Meeting of the British Association for Advancement of Science, 1854, p. 67. See also Liebig and Kopp's *Jahresbericht*.

assert that a certain amount of such separation may not under some circumstances occur. The method of analysis which I have adopted is not delicate enough, nor will the very conditions of the case itself admit of an accurate determination of this point. My results are, however, as I think, sufficient to show that any tendency towards eliquation which may exist must be very slight, although they do not prove that a small amount of it may not be produced by gravity, or by some other force acting against the comparatively feeble affinity of the metals for each other. Experiments upon this subject which have been recorded by previous observers have evidently been exposed either to the error of insufficient mixing in the first instance, or to the loss of zinc by volatilization from those portions of the alloy which were in contact with the air, or to both of these causes. Some of them appear to have also been influenced by the presence of foreign metals in the alloy.

The most contradictory statements have been made by different observers in regard to variations of color among the alloys of copper and zinc. In the specimens which I have myself prepared, no abrupt change, or peculiar modification, of the true color is to be perceived, although some very striking superficial characters present themselves. Starting from the red of pure copper, the color of the alloys is less red and more yellow in proportion as they contain more zinc, until an alloy containing 75 or 80 per cent of copper is reached, the color of which is almost pure yellow; beyond this point, as the proportion of zinc contained in them is increased, the alloys become less yellow, with perhaps a tinge of green, and more white continually, and this by the most gradual stages, until the well-known white alloys are reached. These remarks refer to the color of polished surfaces, as obtained by the use of a fine file. Each of the alloys enumerated in the list upon page 42 having been carefully compared with the chromatic scales of Digeon.*

In several of the alloys, especially in those containing about equal parts of copper and zinc, a beautiful yellow or sometimes gray iridescent film forms upon the surface of the metal during the process of cooling. On fracturing it, moreover, the fibres of which the mass is formed present the same yellowish or grayish iridescence. This is removed at once by filing, when the true color of the alloy is made manifest, as has already been observed by Guettier† in regard to hard-solder. With the exception of Guettier, most modern observers have described this alloy, prepared by fusing

* Cercles Chromatiques de M. E. Chevreul, reproduits au Moyen de la Chromocalcographie, par R. H. Digeon, Paris, 1855. Chez Digeon, Rue Galande, No. 65.

† *Loc. cit.*, S. 207.

together 50 parts copper with 50 of zinc, as being of a deep yellow color; while Karsten* states that it is considerably darker and redder than ordinary brass.† They have evidently all been misled by the superficial coating just described, the color of which is completely analogous to that which occurs upon the crystals of metallic bismuth, now so often to be found in chemical cabinets; or by the color of an almost equally superficial layer of yellow alloy, which forms upon those parts of the ingot which are suddenly cooled. To these changes produced by "tempering" I shall presently again allude. That the surface color is most probably mainly due to oxidation, however, would appear from the fact that not only has the brilliant yellow coating of my specimens of braziers' solder, and of other iridescent alloys, not been dimmed by exposure during several months in a damp cellar, where ordinary polished brass soon became tarnished, but in several instances in which it had been removed by filing, a somewhat similar yellow coat has reappeared after exposure to moist air. Although this iridescence is very strongly marked in the alloy known as braziers' solder, yet an instance perhaps still more striking presented itself in the alloy containing 41.48 per cent of copper. Being very brittle, a specimen of this alloy was accidentally broken into several fragments before it had become thoroughly cold, when a beautiful, glittering iridescent film of a light yellow color at once formed upon its surface. As the alloy was very compact and fine-grained, it could at first sight hardly be believed that the coloration was only superficial; but on breaking the mass after it had become cold, its true color was found to be a very light gray, — indeed, almost white, — as was also proved by filing off a portion of the yellow film. The ingot obtained from the liquid portion of this alloy, having been suddenly cooled, was nearly white, and presented no appearance of iridescence. Upon its under surface, however, which had been instantly solidified by contact with the cold stone upon which it was poured, a thin layer of yellow, malleable, *tempered* alloy was found. In another instance, the ingot obtained from a white alloy containing about 30 per cent of copper having been broken while still warm, the fractured surface instantly assumed a permanent bright

* *Loc. cit.*, S. 394.

† When a piece of solder is heated gradually, it assumes at first a light red color, which subsequently passes to violet, or even to blue violet; a beautiful play of colors, alternating between green, yellow, and violet, succeeds, as the temperature becomes more elevated, until at length, after the lapse of some time, the specimen becomes tarnished with a thick, dull coating of oxide. Since in the founderies where it is prepared this alloy is often taken directly from the ingot-moulds and pounded to powder without having first been allowed to cool, the observation of Karsten admits of ready explanation.

blue-violet color. Indeed, it would appear as if, by properly regulating the process of cooling, a series of colors as varied as those assumed by steel, according to the different degrees of heat at which it is tempered, might be obtained. Alloys containing about 45 per cent of copper exhibit a dull gray coloration on fracture, which, combined with their other physical properties, often causes them, when unpolished, to resemble, as was remarked by Karsten,* metallic sulphides far more than metals.

Although the iridescence which I have described is perhaps seen to best advantage in the alloy from equal parts of copper and zinc, and may perhaps be produced most readily upon it and the neighboring alloys of a fibrous texture, it is by no means confined to these. I have noticed beautiful yellow coatings upon alloys containing 60, 53, and particularly on the one of 90.77 per cent of copper. It may probably occur upon any of the yellow alloys, and is doubtless produced at will upon some of them by manufacturers of ornamental brass castings.

In this connection, it may be mentioned that the color of the oxidized surface of the thin sheets of alloy obtained by pouring upon stone varies from a grayish black, tinged with blue, in the specimens containing about 90 per cent of copper, to a dirty dark yellowish-green, as in the alloy of 65 per cent of copper; and from a dull lead color (alloy of 38.5 per cent of copper) nearly to white, in the alloys rich in zinc.†

Marked changes, not only of color, but also in other of the physical properties of some of these alloys, may be produced by varying the conditions in which they pass from the liquid to the solid state. These changes are very peculiar, and are evidently of great importance, not only in their practical bearing, but also from affording another instance of the phenomena of "tempering," which may possibly be of consequence in the study of this most difficult subject.

In preparing the white alloys containing less than 45 per cent of zinc, I have

* *Loc. cit.*, S. 396.

† Observations upon the color of the alloys of copper and zinc which accord very nearly with my own are those of Guettier (Dingler's Polytech. J., CXIV. 204, (from the *Moniteur Industriel*, 1848), and of Lewis (Chemical Works of C. Naumann, Abridged and Methodized, with Additions, by W. Lewis, (London, 1759,) p. 65), who long ago wrote: "The proportion of Calamine and the increase which the Copper receives from it are different in different works: hence the deeper or paler colour of Brass. I have observed in a large set of experiments on this subject that a little of the Calamine, that is, of the Zinc contained in Calamine, dilutes the colour of the Copper and renders it pale; that when the Copper has imbibed about one twelfth its own weight, the colour inclines to yellow; that the yellowness increases more and more till the proportion comes almost to one half; that on further augmenting the Calamine, the Brass becomes paler and paler, and at last white."

frequently observed, upon the under surface of the sheet obtained by pouring off the liquid alloy, a thin layer of a soft, tenacious, malleable alloy, of a yellow color. The formation of this singular sheet was at first attributed to eliquation; but as it was difficult to conceive that an alloy apparently richer in copper should remain at the surface of the melted mass in the crucible, — which must have been the case in order that it should form the bottom of the ingot, — it was thought possible that volatilization of the zinc might have increased the proportion of copper at the surface of the melted alloy. In order to decide this question, a new series of alloys was prepared, extending from the one obtained by melting together 40 parts of copper plus 60 parts of zinc, to the mixture of 56 parts of copper and 44 parts of zinc; — each alloy being made from a mixture containing one per cent more copper than that used in preparing the preceding. After thorough stirring, the alloys were cast into ingots of about five pounds' weight. In the first four of these alloys — from 40 to 44 per cent of copper — the yellow film was very clearly defined on the three sides of the ingot which had come in contact with the metal of the mould, while on the upper surface of the ingot, which had cooled in contact with the air, no trace of it could be detected. This yellow film is usually of extreme tenuity, hardly exceeding one sixteenth of an inch in thickness in any of the instances which I have observed. It is, however, so very clearly defined in the white alloys containing 40 to 45 per cent of copper, being readily bent, cut, or filed, while the remainder of the alloy is exceedingly hard and brittle, that no question as to its identity can possibly be entertained. In the alloys containing more than 50 per cent of copper, which are naturally of a yellow color, it is not so easy to detect a similar film. In the series of ingots just mentioned, it could nevertheless be traced as far up as the alloy prepared from 54 parts of copper plus 46 parts of zinc.

An experiment made in order to ascertain whether this soft modification of the alloys could be obtained at will, afforded no positive result. An alloy of 42 parts of copper plus 58 parts of zinc being prepared, a portion of it was poured by small drops into a large mass of cold water. The surfaces of many of the granules thus obtained were covered with a yellow film, and this was especially true of the smallest pieces; but the film was exceedingly thin, and the interior of the granules consisted entirely of brittle white alloy. Other portions were thrown out upon cold iron plates, so as to form very thin sheets. A thin yellow film occurred, it is true, upon the inferior surfaces of these sheets, but above it the alloy was white and brittle. Another portion of the melted alloy was cast in an iron ingot-mould which had previously been heated "black-hot." The yellow film was still formed

where the alloy came in contact with the ingot-mould; it was, however, exceedingly thin. On pouring some of the remaining alloy into a cold iron mould, a yellow film of the usual thickness was obtained.

Although the phenomena of tempering exhibited by these alloys are more readily perceived among those the normal color of which is white, it is highly probable that all the alloys are liable to have their physical properties influenced to a greater or less extent from this cause. This would appear, not only from the evident analogy of these phenomena with those which are known to occur with alloys of copper and tin;* but Dussaussoy† has already shown that ordinary brass, copper 65 to 70 per cent plus zinc 30 to 35 per cent, is rendered softer, less tenacious, and less dense by tempering it;—a fact which Mallet‡ has very properly urged in explanation of the differences between several of the specific gravities of alloys of copper and zinc observed by himself, and the numbers which had been previously obtained by other experimenters. I would here suggest that it explains equally well the very great variations among the specific gravities of the different alloys studied by Mallet himself.§ It is also the most probable explanation of the alloys of abnormal color which he has described. I should observe in this connection, that in the alloys of light yellow color the yellow appears to be made much deeper when the alloy is strongly compressed, as when cut with a cold-chisel or hammered. I may also incidentally mention, that in the series of alloys which I have prepared, a constantly increased degree of hardness has been observed, in proportion to the amount of zinc contained in the alloy,—at least as far as the brittle white alloys, which are so hard that an ordinary file makes little or no impression upon them;|| a result

* *Vid.* d'Arcet in *Dictionnaire de l'Industrie Manufacturière, etc.*, X. 500, Art. *Tam-tam* (Paris, Baillière, 1841); also, *Ann. Ch. et. Phys.*, (2.) LIV. 331. See also Dussaussoy, *Ann. Ch. et. Phys.*, (2.) V. 225.

† *Loc. cit.*, p. 226, et *Tableau* No. 5.

‡ *Loc. cit.*, p. 264.

§ I have found it impossible to construct a curve of any regularity from the observations of this chemist, although it is tolerably clear that the greatest condensation is at a point somewhere below the alloy composed of equal equivalents of copper and zinc, and that between this point and pure copper the specific gravity gradually increases with some degree of regularity in proportion as the amount of copper increases. Among the observed specific gravities of the white alloys rich in zinc, there is no regularity whatsoever. The determinations of Mallet are, nevertheless, unquestionably the best which have ever been made; possibly they are the best which could be made in any case. At all events, few chemists are in the position to improve upon the method of preparing alloys which was employed by this distinguished observer.

|| From this category the alloys modified by tempering must of course be excepted.

which agrees with those of Karsten,* of Mallet,† and of Guettier.‡ Calvert and Johnson§ have recently attempted to express these differences numerically. The alloy containing 54 per cent of copper, which is still so tenacious that small bits cannot readily be broken from it, was found to be exceedingly difficult to cut with a cold-chisel; for though still so soft that it could be filed without any very great trouble, it destroyed at once the edges of cutting instruments, though the latter were well tempered. This peculiarity appears to be connected with the fibrous structure of the alloy.

In conclusion, I must express my gratitude to my friend, Professor J. P. Cooke, of Cambridge, who has kindly invited me to make use of the admirable laboratory in which this research has been conducted. By his suggestion, moreover, my attention was first directed to the subject. Nor can I omit to mention the fact, that I am indebted to Messrs. J. Davis, Jr. and John Revere, officers of the Revere Copper Company of Boston, for the gratuitous use of the large quantities of metal which I have employed. I have also been permitted by them to make free use of the furnaces and other appliances in the extensive founderies of the company. For the valuable aid and uniform kindness of these gentlemen, I would here return my warmest thanks.

* *Loc. cit.*, S. 393.

† *Loc. cit.*, *passim*.

§ *Loc. cit.*, p. 199.

‡ *Loc. cit.*, p. 307; also Gmelin's Handbook, (Cavendish Soc. Edit.,) V. 479.

HARVARD COLLEGE LABORATORY,

September 1st, 1859.